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(54) **Aramid filament yarn provided with a conductive finish**

(57) The invention pertains to an aramid filament yarn provided with > 1.5 wt.% of a finish comprising an organic substance with a conductivity of > 4 mS/cm, measured as a 50 wt.% finish composition in water at

20°C, having a specific electric resistance of the yarn < 2.5.10⁴ Ohm.cm, and to a method of making said yarn.

EP 1 435 407 A1

Description

[0001] The invention pertains to an aramid filament yarn provided with a conductive finish, to a method of making such yarn, and to the use of said yarn.

[0002] A common problem of yarns is breaking of the yarn when used in certain applications. Yarn breaks may occur as a result of over-loading, fatigue, or wear. Ground cable damage may also occur as a result of damage caused by rodents. In elevator cables breakage of cables is a serious safety problem. It is known to add to aramid reinforced elevator cables, for example, one or more carbon yarns or metal wire as a break detector. Such treated aramid reinforced cables, however, do not have the same mechanical characteristics as cables made of untreated aramid yarns only. Moreover, the breaking characteristics of such carbon yarn or metal wire is different from the breaking characteristics of aramid yarn, thereby hampering accurate indication of breaking danger of the aramid reinforced cable. The other mechanical properties of non-aramid yarns in comparison to the main reinforcing material of the cable complicates the predictability of a cable breakage considerably. It would be an advantage to provide aramid yarn having sufficient conductive properties and nevertheless having the same mechanical characteristics as the untreated aramid yarns in the cable.

[0003] Some solutions to the above problems are proposed. In WO 9748832 the yarn was coated with a metal such as nickel with an acid. Such treatment provides metalized yarns, the fiber surfaces of which may be damaged by the acid treatment, leading to decrease of tenacity and/or elongation properties. In WO 9325748 a process was disclosed for treating aramid fibers with a dispersion of particulate graphite material in a swelling solvent. Also using this method bears the risk of damaging the fiber surface. Moreover, both methods are very complicated, time consuming, and therefore costly.

[0004] The present invention therefore provides in a solution of the above problems, using a simple procedure that is no time consuming, cheap, and without any risk of damaging the fibers. It was found that an aramid filament yarn provided with a finish comprising > 1.5 wt.% of an organic substance with a conductivity of > 4 mS/cm, measured as a 50 wt.% finish composition in water at 20°C, having a specific electric resistance of the yarn < 2.5.10⁴ Ohm.cm, possesses a sufficient conductivity to be used as a breaking detector, without affecting its mechanical properties. This is a substantial advantage over the use of, for example, a carbon yarn or a metal wire as break detector in aramid reinforced elevator cables. The conductivity of the organic substance treated and damaged yarn is reduced as a result of breaks caused by wear or fatigue and provides information to the user on the remaining lifetime of the cable. The conductivity of a yarn or a cable can be determined with a resistancy or multimeter.

When finishes comprising a conductive organic substance (COS) are applied onto aramid filament yarn, the electrical yarn resistance thereof is reduced. Depending on the amount of finish and on the conductivity of the applied organic substance, the treated yarn can be used as such, or in combination with untreated aramid filament yarn as an early break detector in (elevator, bearer, ground) cables, or for accessories (brushes, rollers) which have to lay on or to eliminate static electricity in, for example, record players, magnetic tapes, compact disks, and the like.

The conductive organic substance can be applied onto wet or dried yarn as a spin-finish (before or after the drying, as such or diluted with a solvent such as water) in the spinning process or in a separate process step at a relatively high yarn speed.

[0005] Aramid filament yarns treated with > 2 wt. % of a conductive organic substance with a conductivity of > 30 mS/cm are preferred. More preferred are yarns treated with > 2 % of a conductive organic substance with a conductivity of > 41 mS/cm. The specific electric resistance of the yarn is preferably < 2.10³ Ohm.cm, more preferably < 10³ Ohm.cm. particularly suitable amounts of COS are within the range 3 to 12 wt.%, more preferably within the range 4-9 wt.%. The wt.% is relative to the total weight of the yarn without finish.

[0006] Suitable organic substances that are suitable for use in the invention are salts or materials having statically chargeable acid or base groups. Materials with acid groups have preferably carboxylate, phosphonate or sulfonate groups. Materials with base groups have preferably amine groups.

Particularly preferred materials are fatty acids, carbonic acids, (cyclo)alkyl phosphates, (cyclo)alkyl phosphonates, (cyclo)alkyl sulfates, (cyclo)alkyl sulfonates, imidazoline derivatives and polymers such as poly(diallyldimethylammonium chloride), and the like.

[0007] The aramid yarns preferably are made of poly(p-phenylene terephthalamide) (PPDT), but may also contain minor amounts of other monomers.

[0008] The COS is applied onto the yarn by conventional methods known in the art. The COS can be applied in solution. The solvent may be any suitable solvent, such as alcohol, ether, tetrahydrofuran, acetone, benzene, toluene, ethyl acetate, dichloromethane and the like. Most preferably the COS is applied as an aqueous solution. Some COS's are purchased as a water-containing product that can be applied as such.

[0009] The suitable amount of COS to be applied can very easily be determined by a simple conductivity measurement, which as such is known in the art. When the conductivity of the COS or the solution of the COS is determined, a skilled person can easily apply the required amount of finish as needed for the specific use.

Procedure for the determination of the conductivity of a finish

[0010] A suitable procedure to determine the conductivity of a finish composition according to the invention is as follows.

A sufficient amount of the aqueous finish solution (50 wt.% of water and 50 wt.% of COS) to be tested is poured into a beaker. Subsequently, the conductivity of this solution is determined according DIN norm 38404 Teil 8 (9.1985) at a temperature of 20°C.

When the finish containing the COS has a lower or higher water content than 50 wt.%, the concentration of the finish solution should be adjusted to 50 wt.% by respectively the addition of demineralized water or the evaporation of water by heating on a hot plate under stirring at an elevated temperature below 100°C. For the measurement of the conductivity a conductivity meter type LF 537 of the Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany was used.

The water content of the finish solution was determined by the Karl Fischer method. An exact description of the determination of water via Karl Fischer reagent is given in "Karl Fischer Titration, Methoden zur Wasserbestimmung" by Eugen Scholz, Springer-Verlag 1984.

Procedure for the determination of the specific electrical resistance

[0011] For the determination of the specific electrical resistance of the aramid yarns a sample-holder consisting of two copper bars separated by two polytetrafluorethylene rods was used. The mutual distance of the bars is 52 mm. The yarn to be tested is wound a number of times (preferably between 3 and 7) times around the two copper bars which are connected with a DC high voltage power source and a Keithley electrometer. With the Keithley electrometer the electrical current was determined after a voltage of 500 V was applied over the copper bars at 20°C and 65% relative humidity. The specific electrical resistance of the yarn was calculated based on Ohm's law, the yarn length between the copper bars, the number of yarn connections, and the cross-section area of the yarn.

[0012] The invention is further illustrated with the following non-limitative examples.

Example 1

[0013] This example illustrates the procedure of applying a finish containing a conductive organic substance (COS) to a wet, not previously dried, yarn in an operation integrated with the spinning process. A spinning mass was prepared by mixing concentrated (99.8 wt.%) sulfuric acid snow with powdered poly-p-phenylene terephthalamide. The spinning mass was de-aerated, heated to 90°C in a double-screw extruder and fed to a spinneret via a filter and a spinning pump. The spinneret had 1000 orifices of 59 micrometer in diameter. The spinning mass was extruded through the spinning orifices and thereafter successively passed through an air zone of 8 mm in length and a coagulation bath. This bath was a dilute solution of sulfuric acid in water (about 19% by weight) having a temperature of 5°C. The filament bundle thus formed successively passed through a neutralization bath containing a dilute sodium carbonate solution and a washing bath in which the filaments were thoroughly washed with water of about 75°C. Excess adhering water was removed with the aid of a squeeze roller pair. Next, the non-dried bundle of filaments was provided with an aqueous finish containing a COS with the aid of a liquid applicator and a feed pump. Next the yarn was passed over a series of 3 drying drums (6 wraps of 160°C, 6 wraps of 180°C, 4 wraps of 200°C). The yarn was in contact with the surface of the drums for 5-6 seconds in all. Subsequently, the yarn was passed over a transport drum (4 wraps of about 20°C) and was wound into a package at a speed of 400 m/min. The yarn obtained had a linear density of 1610 dtex. The following process conditions were varied (table A and B):

- a) the composition of the finish containing the COS
- b) the amount of COS on yarn

Table A

Aqueous finishes containing conductive organic substances				
Finish concentration in wt.%	Finish composition code			
	a1 20	b1 20	c1 20	d1 20
COS in solution (%)				

EP 1 435 407 A1

Table A (continued)

Aqueous finishes containing conductive organic substances				
Finish concentration in wt. %	Finish composition code			
	a1 20	b1 20	c1 20	d1 20
Afilan V4855 (37.6%)	53,2	37,2		
Afilan PTU		6,0		
PolyDADMAC (42.4%)			47,1	
Tallopol ACF (50.5%)				39,6
Demineralized water	46,8	56,8	52,9	60,4

Afilan V4855 is an alkane phosphonate, potassium salt, ex-Clariant GmbH, Frankfurt, Germany.
Afilan PTU is an ethoxylated and propoxylated oleic acid, CH₃-capped, ex-Clariant GmbH, Frankfurt, Germany.
PolyDADMAC is the abbreviation of poly(diallyldimethylammonium chloride) with a low mol weight; catalog nr. 52237-6, supplier Aldrich Chemical Company, Inc., Milwaukee, USA.
Tallopol ACF is a product mixture of potassium and sodium salts of carbonic acids, ex-Stockhausen, Krefeld, Germany.

Table B

The specific electrical resistance					
Experiment No.	1A	1B	1C	1D	1E
Finish composition applied with applicator	a1	b1	b1	c1	d1
COS amount on yarn (wt.%)	3,0	3,0	4,0	4,0	4,0
Conductivity of a 50 wt. % finish composition in mS/cm at 20°C	42,6	43,7	43,7	45,4	215,0
Specific electrical resistance of the yarn in Ohm.cm	3,5E+03	6,5E+03	2,8E+03	2,8E+03	5,8E+02

Comparative Example 1

[0014] This comparative example relates to an experiment in which the yarn of Example 1 was provided with 0.9% of a non-ionic finish normally used for the spinning of Twaron® yarns. The conductivity of the finish solution (50 wt.%) was 0.009 mS/cm. The obtained yarn showed a specific electrical resistance of 7.2E+07 Ohm.cm.

Example 2

[0015] This example illustrates the procedure of applying a finish containing a conductive organic substance (COS) to a dried yarn in an operation integrated with the spinning process. The spinning mass of Example 1 was extruded through a spinneret which had 2000 orifices of 59 micrometer in diameter and was thereafter successively passed through the same air zone, coagulation, neutralization, and washing bath as described in Example 1. Excess adhering water was removed with the aid of a squeeze roller pair. Next, the yarn was passed over a series of 3 drying drums (6 wraps of 160°C, 6 wraps of 180°C, 4 wraps of 250°C). The yarn was in contact with the surface of the drums for about 7 seconds in all. Next, the completely dried bundle of filaments was provided with an aqueous finish containing a COS with the aid of a liquid applicator and a feed pump. Subsequently, the yarn was passed over a transport drum (4 wraps of about 20°C) and was wound into a package at a speed of 300 m/min. The yarn obtained had a linear density of 3220 dtex. The following process conditions were varied (table C and D):

- a) the composition of the finish containing the COS
- b) the amount of COS on yarn
- c) the concentration of the finish solution

Table C

Aqueous finishes containing conductive organic substances			
Finish concentration in wt.%	Finish composition code		
	a2 37,6	b2 46,3	d2 50
COS in solution (%)			
Afilan V4855 (37.6%)	100,0	86,1	
Afilan PTU		13,9	
Tallopol ACF (50.5%)			99,0
Demineralized water			1,0

Table C

The specific electrical resistance			
Experiment No.	2A	2B	2C
Finish composition applied with applicator	a2	b2	d2
COS amount on yarn (wt.%)	3,0	3,5	2,5
Conductivity of a 50 wt.% finish composition in mS/cm at 20°C	42,6	43,7	215,0
Specific electrical resistance of the yarn in Ohm.cm	7,8E+03	7,2E+03	9,6E+02

Example 3

[0016] This example illustrates the application of a finish containing a conductive organic substance (COS) to a dried yarn not directly coupled to the spinning process. Commercially available Twaron® 2200 (1610 dtex/f 1000) yarn was subjected to the following treatments. The yarn package was rollingly unwound while successively passing the yarn over a liquid applicator, through a steam box (temperature 240°C, residence time 8 seconds) and finally wound into a package at a speed of 75 m/min. With the liquid applicator and a feed pump, the yarn was coated with the finishes mentioned in table E and F. The following process conditions were varied:

- a) the composition of the finish containing the COS
- b) the amount of COS on yarn
- c) the concentration of the finish solution

Table E

Aqueous finishes containing conductive organic substances				
Finish concentration in wt.%	Finish composition code			
	a3 15	d3 10	d4 15	d1 20
COS in solution (%)				
Afilan V4855 (37.6%)	40,0			
Tallopil ACF (50.5%)		19,8	29,7	39,6
Demineralized water	60,0	80,2	70,3	60,4

Table F

The specific electrical resistance				
Experiment No.	3A	3B	3C	3D
Finish composition applied with applicator	a3	d3	d4	d1
COS amount on yarn (wt.%)	2,5	2,0	3,0	4,0
Conductivity of a 50 wt.% finish composition in mS/cm at 20°C	42,6	215,0	215,0	215,0
Specific electrical resistance of the yarn in Ohm.cm	3,9E+03	2,9E+03	1,8E+03	8,8E+02

Example 4

[0017] This example illustrates the application of a finish containing a conductive organic substance (COS) to a dried yarn not directly coupled to the spinning process. Commercially available Twaron® 2200 (3220 dtex/f 2000) yarn was subjected to the following treatments. The yarn package was unwound while successively passing the yarn over a double rotating kiss-roll and through a hot air oven (temperature 180°C, residence time 18 seconds) and was finally wound into a package at a speed of 100 m/min. With the double kiss-roll the yarn was coated with the finishes mentioned in table G and H. The following process conditions were varied:

- a) the composition of the finish containing the COS
- b) the amount of COS on yarn
- c) the concentration of the finish solution

Table G

Aqueous finishes containing conductive organic substances		
Finish concentration in wt.%	Finish composition code	
	a1 20	d4 15
COS in solution (%)		
Afilan V4855 (37.6%)	53,2	
Tallopul ACF (50.5%)		29,7
Demineralized water	46,8	70,3

Table H

The specific electrical resistance		
Experiment No.	4A	4B
Finish composition applied with applicator	a1	d4
COS amount on yarn (wt.%)	10,3	5,6
Conductivity of a 50 wt.% finish composition in mS/cm at 20°C	42,6	215,0
Specific electrical resistance of the yarn in Ohm.cm	3,5E+03	1,2E+03

Example 5

[0018] This example illustrates the application of a finish containing a conductive organic substance (COS) to a dried

and finish-free yarn not directly coupled to the spinning process. A package of finish-free Twaron® (1610 dtex/f 1000) yarn was subjected to the following treatments. The yarn package was unwound while successively passing the yarn over a liquid applicator, through a hot air oven (temperature 90°C, residence time 32 seconds) and was finally wound into a package at a speed of 50 m/min. With the liquid applicator and a feed pump, the yarn was coated with the finishes mentioned in table K and L. The following process conditions were varied:

- a) the composition of the finish containing the COS
- b) the amount of COS on yarn
- c) the concentration of the finish solution

Table K

Aqueous finishes containing conductive organic substances			
Finish concentration in wt.%	Finish composition code		
	e1 20	f1 32	g1 20
COS in solution (%)			
Leomin AN	20,0	16,0	
Leomin OR		16,0	
Atlas G3634a			20,0
Demineralized water	80,0	68,0	80,0
Leomin AN is an ethyl octane phosphonate, potassium salt; ex Clariant GmbH, Frankfurt, Germany. Leomin OR is a polyglycol ester of a fatty acid, ex Clariant GmbH, Frankfurt, Germany. Atlas G3634a is an imidazoline derivate, quarternized, ex Uniqema, Middlesbrough, England.			

Table L

The specific electrical resistance			
Experiment No.	5A	5B	5C
Finish composition applied with applicator	e1	f1	g1
COS amount on yarn (wt.%)	5,0	8,0	5,0
Conductivity of a 50 wt.% finish composition in mS/cm at 20°C	40,8	15,2	4,7
Specific electrical resistance of the yarn in Ohm.cm	2,2E+03	5,6E+03	2,2E+04

Claims

1. An aramid filament yarn provided with a finish comprising > 1.5 wt.% of an organic substance with a conductivity of > 4 mS/cm, measured as a 50 wt.% finish composition in water at 20°C, having a specific electric resistance of the yarn < 2.5.10⁴ Ohm.cm.
2. The aramid filament yarn of claim 1 provided with a finish comprising > 2 wt.% of an organic substance with a conductivity of > 30 mS/cm, measured as a 50 wt.% finish composition in water at 20°C, having a specific electric resistance of the yarn < 2.10³ Ohm.cm.
3. The aramid filament yarn of claim 1 or 2 provided with a finish comprising > 2 wt.% of an organic substance with a conductivity of > 41 mS/cm, measured as a 50 wt.% finish composition in water at 20°C, having a specific electric resistance of the yarn < 10³ Ohm.cm.

EP 1 435 407 A1

4. A method of making the yarn of claim 1 having a specific electric resistance of the yarn $< 2.5 \cdot 10^4$ Ohm.cm, comprising bringing a solution of an organic substance onto the aramid yarn such as to obtain > 1.5 wt.% of the substance relative to the total weight of the yarn without the finish, **characterized in that** the organic substance has a conductivity of > 4 mS/cm, measured as a 50 wt.% finish composition in water at 20°C.

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5. Use of the yarn of claim 1 in conductive aramid-containing materials.

6. Use of the yarn of claim 1 in lift cables.

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7. Use of the yarn of claim 1 in fibers for transporting electric current or for eliminating static electricity.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 00 0120

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 478 648 A (STEIN GERHARD ET AL) 26 December 1995 (1995-12-26)	1-5,7	D06M13/292
Y	* column 1, line 43 - column 2, line 64 *	6	D06M13/17
	---		D06M15/53
Y	US 5 834 942 A (DE ANGELIS CLAUDIO) 10 November 1998 (1998-11-10)	6	D06M15/356
	* column 1, line 52 - line 62 *		D06M11/76
	* column 2, line 15 - line 62 *		D06M13/352
	---		B66B7/12
X	US 5 674 615 A (NEUERT RICHARD ET AL) 7 October 1997 (1997-10-07)	1-5,7	B66D1/54
	* column 1, line 43 - column 2, line 14 *		B66B5/00
	* column 6, line 35 - line 41 *		D07B1/14

X	EP 0 416 486 A (DU PONT) 13 March 1991 (1991-03-13)	1,4,5,7	
	* page 4, line 24 - page 5, line 42 *		

X	WO 92 15747 A (DU PONT) 17 September 1992 (1992-09-17)	1,4,5,7	
	* page 2, line 11 - page 3, line 32 *		
	* page 8, line 4 - line 7 *		

A	EP 0 423 703 A (DU PONT) 24 April 1991 (1991-04-24)	1-7	
	* page 2, line 33 - line 40 *		

The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		21 August 2003	Fiocco, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (03.82) (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 0120

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-08-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5478648	A	26-12-1995	DE	4402193 C1	01-06-1995
			EP	0665323 A2	02-08-1995
			JP	7229059 A	29-08-1995

US 5834942	A	10-11-1998	AT	181977 T	15-07-1999
			AU	700649 B2	14-01-1999
			AU	4584896 A	19-09-1996
			BR	9600892 A	30-12-1997
			CA	2169431 A1	07-09-1996
			CN	1134484 A ,B	30-10-1996
			CZ	9600649 A3	11-09-1996
			DE	59602355 D1	12-08-1999
			DK	731209 T3	17-01-2000
			EP	0731209 A1	11-09-1996
			ES	2136335 T3	16-11-1999
			HK	1011391 A1	28-04-2000
			HU	9600548 A2	28-05-1997
			JP	8261972 A	11-10-1996
			NO	960880 A	09-09-1996
			NZ	286035 A	24-06-1997
			PL	313088 A1	16-09-1996
			RU	2148117 C1	27-04-2000
			TR	960867 A2	21-10-1996
			ZA	9601733 A	10-09-1996

US 5674615	A	07-10-1997	DE	4410708 C1	13-07-1995
			EP	0675222 A2	04-10-1995

EP 0416486	A	13-03-1991	DE	3929376 C1	18-04-1991
			AU	619695 B2	30-01-1992
			AU	6214790 A	14-03-1991
			BR	9004398 A	10-09-1991
			CA	2024268 A1	06-03-1991
			CN	1050573 A	10-04-1991
			DE	69007909 D1	11-05-1994
			DE	69007909 T2	25-08-1994
			EP	0416486 A2	13-03-1991
			ES	2063220 T3	01-01-1995
			IE	903202 A1	13-03-1991
			JP	2893652 B2	24-05-1999
			JP	3104929 A	01-05-1991
			KR	138982 B1	15-05-1998
			NO	903857 A	06-03-1991
			TR	24686 A	01-03-1992
			US	5139873 A	18-08-1992
			US	5270113 A	14-12-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 0120

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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21-08-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0416486	A	ZA 9007071 A	27-05-1992
-----	-----	-----	-----
WO 9215747	A	17-09-1992	CN 1076977 A ,B 06-10-1993
		DE 4106682 A1	08-10-1992
		AU 660455 B2	29-06-1995
		AU 1460892 A	06-10-1992
		BR 9205704 A	02-08-1994
		DE 69200321 D1	15-09-1994
		DE 69200321 T2	09-02-1995
		EP 0574507 A1	22-12-1993
		ES 2057991 T3	16-10-1994
		JP 3383860 B2	10-03-2003
		JP 6505312 T	16-06-1994
		WO 9215747 A1	17-09-1992
		US 5270113 A	14-12-1993
		CA 2105092 A1	03-09-1992
		KR 215686 B1	16-08-1999
-----	-----	-----	-----
EP 0423703	A	24-04-1991	AU 629993 B2 15-10-1992
		AU 6465690 A	18-04-1991
		BR 9005205 A	17-09-1991
		CA 2027661 A1	17-04-1991
		CN 1051770 A	29-05-1991
		EP 0423703 A2	24-04-1991
		IE 903679 A1	24-04-1991
		JP 3185180 A	13-08-1991
		NO 904449 A	17-04-1991
		PT 95604 A	30-09-1991
-----	-----	-----	-----